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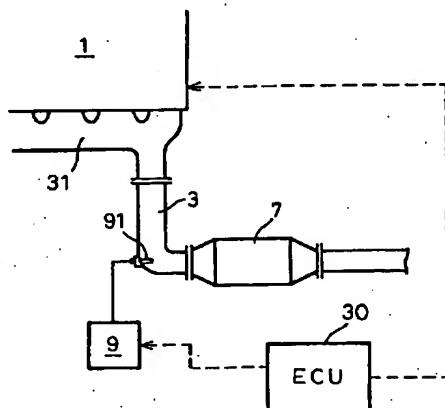
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(54) 【発明の名称】 内燃機関の排気浄化装置

(57) 【要約】

【課題】 NO<sub>x</sub> 吸収還元触媒のNO<sub>x</sub> 済化率を向上させる。  
【解決手段】 機関1の排気通路3にNO<sub>x</sub> 吸収還元触媒7を配置してリーン空燃比運転中の機関の排気に含まれるNO<sub>x</sub> を吸収し、触媒7のNO<sub>x</sub> 吸収量が予め定めた判定値に到達したときに、触媒7上流側の排気通路に還元剤供給ノズル91から還元剤(ディーゼル油)を噴射して触媒7からNO<sub>x</sub> を放出、還元浄化する。上記判定値は、還元剤供給開始直後のNO<sub>x</sub> 吸収還元触媒からの吐き出しによる未浄化NO<sub>x</sub> 放出量、またはNO<sub>x</sub> 吸収中の染み出しによる未浄化NO<sub>x</sub> 放出量が予め定めた低い値になるように設定される。これにより、吸収NO<sub>x</sub> 量の増大による吐き出しありは染み出しによる未浄化NO<sub>x</sub> 放出が低い値に抑制されるため、NO<sub>x</sub> 吸収還元触媒の全体としてのNO<sub>x</sub> 浈化率が大幅に向上する。

図 1



- 1…ディーゼル機関  
3…排気通路  
7…NO<sub>x</sub> 吸収還元触媒  
9…還元剤供給装置  
30…電子制御ユニット  
91…還元剤供給ノズル

## 【特許請求の範囲】

【請求項1】 内燃機関の排気通路に配置され流入する排気の空燃比がリーンのときに排気中のNO<sub>x</sub>を吸収し、流入する排気中の酸素濃度が低下したときに吸収したNO<sub>x</sub>を放出するNO<sub>x</sub>吸蔵還元触媒と、該NO<sub>x</sub>吸蔵還元触媒に流入する排気空燃比がリーンのときにNO<sub>x</sub>吸蔵還元触媒に還元剤を供給することにより、NO<sub>x</sub>吸蔵還元触媒に流入する排気中の酸素濃度を低下させるとともに、放出されたNO<sub>x</sub>を還元浄化する還元剤供給装置とを備えた内燃機関の排気浄化装置において、前記NO<sub>x</sub>吸蔵還元触媒は、前記還元剤供給開始直後に、供給された還元剤によっては還元されない未浄化NO<sub>x</sub>を下流側に放出し、該未浄化NO<sub>x</sub>量はNO<sub>x</sub>吸蔵還元触媒の吸収したNO<sub>x</sub>量に応じて増加し、前記還元剤供給装置は、NO<sub>x</sub>吸蔵還元触媒に吸収されたNO<sub>x</sub>量が所定のレベルに到達したときにNO<sub>x</sub>吸蔵還元触媒に還元剤を供給し、前記所定のNO<sub>x</sub>吸收量レベルは、前記還元剤供給開始時の前記NO<sub>x</sub>吸蔵還元触媒からの未浄化NO<sub>x</sub>放出量が予め定めた値以下になるように設定されていることを特徴とする内燃機関の排気浄化装置。

【請求項2】 内燃機関の排気通路に配置され流入する排気の空燃比がリーンのときに排気中のNO<sub>x</sub>を吸収し、流入する排気中の酸素濃度が低下したときに吸収したNO<sub>x</sub>を放出するNO<sub>x</sub>吸蔵還元触媒と、該NO<sub>x</sub>吸蔵還元触媒に流入する排気空燃比がリーンのときにNO<sub>x</sub>吸蔵還元触媒に還元剤を供給することにより、NO<sub>x</sub>吸蔵還元触媒に流入する排気中の酸素濃度を低下させるとともに、放出されたNO<sub>x</sub>を還元浄化する還元剤供給装置とを備えた内燃機関の排気浄化装置において、前記NO<sub>x</sub>吸蔵還元触媒は、流入する排気空燃比がリーンであっても吸収したNO<sub>x</sub>量に応じて増大する量の未浄化のNO<sub>x</sub>を下流側に放出し、前記還元剤供給装置は、NO<sub>x</sub>吸蔵還元触媒に吸収されたNO<sub>x</sub>量が所定のレベルに到達したときにNO<sub>x</sub>吸蔵還元触媒に還元剤を供給し、前記所定のNO<sub>x</sub>吸收量レベルは、リーン空燃比排気下における前記NO<sub>x</sub>吸蔵還元触媒からの未浄化NO<sub>x</sub>放出量が予め定めた値以下になるように設定されていることを特徴とする内燃機関の排気浄化装置。

【請求項3】 前記還元剤供給装置は、前記NO<sub>x</sub>吸蔵還元触媒の上流側の排気通路に還元剤を噴射する還元剤供給ノズルを備え、NO<sub>x</sub>吸蔵還元触媒に流入する排気空燃比がリーンのときにNO<sub>x</sub>吸蔵還元触媒に吸収されたNO<sub>x</sub>量が前記所定のレベルに到達する毎に予め定めた量の還元剤を排気中に供給する請求項1または請求項2に記載の内燃機関の排気浄化装置。

【請求項4】 前記還元剤供給ノズルからの還元剤の噴射量と噴射率とは、前記還元剤の供給が行われる時間間隔に応じて設定されている請求項3に記載の内燃機関の

## 排気浄化装置。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は内燃機関の排気浄化装置に関し、詳細には流入する排気空燃比がリーンのときに排気中のNO<sub>x</sub>を吸収し、流入する排気中の酸素濃度が低下したときに吸収したNO<sub>x</sub>を放出するNO<sub>x</sub>吸蔵還元触媒を備えた内燃機関の排気浄化装置に関する。

## 【0002】

【従来の技術】流入する排気空燃比がリーンのときに排気中のNO<sub>x</sub>を吸収し、流入する排気中の酸素濃度が低下したときに吸収したNO<sub>x</sub>を放出するNO<sub>x</sub>吸蔵還元触媒が知られている。この種のNO<sub>x</sub>吸蔵還元触媒を用いた内燃機関の排気浄化装置の例としては、例えば特開平6-200738号公報に記載されたものがある。

【0003】同公報の装置は、リーン空燃比で運転可能な機関の排気通路にNO<sub>x</sub>吸蔵還元触媒を配置し、機関がリーン空燃比で運転されているときに排気中のNO<sub>x</sub>を吸収させ、NO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸收量が所定値に到達したときにNO<sub>x</sub>吸蔵還元触媒の上流側の排気通路に配置した還元剤供給ノズルから還元剤として液体または気体の炭化水素等を排気中に噴射するようにしたものである。NO<sub>x</sub>吸蔵還元触媒に排気とともに還元剤が供給されると、還元剤のNO<sub>x</sub>吸蔵還元触媒上の酸化により排気中の酸素濃度が低下するためNO<sub>x</sub>吸蔵還元触媒からは吸収したNO<sub>x</sub>が放出される。また、放出されたNO<sub>x</sub>は触媒上で排気中の還元剤と反応して還元、浄化される。

## 【0004】

【発明が解決しようとする課題】ところが、上記特開平6-200738号公報の装置のように、ある時間間隔でNO<sub>x</sub>吸蔵還元触媒に還元剤を供給してNO<sub>x</sub>吸蔵還元触媒からのNO<sub>x</sub>の放出と還元浄化とを行うようにしたときに、還元剤供給の時間間隔によっては全体としてのNO<sub>x</sub>の浄化率が良好にならない場合が生じる。

【0005】通常、NO<sub>x</sub>吸蔵還元触媒に還元剤を供給してNO<sub>x</sub>吸蔵還元触媒からのNO<sub>x</sub>の放出と還元浄化とを行う操作（以下、「NO<sub>x</sub>吸蔵還元触媒の再生操作」と呼ぶ）は、NO<sub>x</sub>吸蔵還元触媒に吸収されたNO<sub>x</sub>量がある一定レベルに到達したときに実行されるが、このNO<sub>x</sub>吸収量のレベルはNO<sub>x</sub>吸蔵還元触媒が吸収したNO<sub>x</sub>で飽和する吸収量（飽和量）を基準に定められる。すなわち、NO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸収能力を最大限に活用してNO<sub>x</sub>吸蔵還元触媒の再生操作の実行頻度を低く抑えるためには、できるだけ多くのNO<sub>x</sub>がNO<sub>x</sub>吸蔵還元触媒に吸収されてから再生操作を実行することが好ましい。そこで、通常、再生操作を実行するNO<sub>x</sub>吸収量のレベルはNO<sub>x</sub>吸蔵還元触媒の飽和量にある程度の余裕を見た比較的高いレベル（例えばNO<sub>x</sub>吸蔵還元触媒の飽和量の70バーセント程度）に設定

される。

【0006】ところが、このようにNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸収量が比較的高いレベルに到達するまで待つてNO<sub>x</sub>吸蔵還元触媒の再生操作を実行した場合には全体としてのNO<sub>x</sub>の浄化率を大幅に向上去ることが困難であることが判明している。例えば、従来NO<sub>x</sub>吸蔵還元触媒の再生操作時にはNO<sub>x</sub>吸蔵還元触媒から放出されたNO<sub>x</sub>は供給された還元剤により完全に浄化され、下流側には未浄化のNO<sub>x</sub>は放出されないと考えられていた。ところが、実際にはNO<sub>x</sub>吸蔵還元触媒の再生操作時に未浄化のままのNO<sub>x</sub>が触媒下流側に放出される場合があることが判明している。

【0007】前述のように、還元剤が供給されるとNO<sub>x</sub>吸蔵還元触媒近傍の酸素濃度が低下しNO<sub>x</sub>吸蔵還元触媒からはNO<sub>x</sub>が放出される。ところが、触媒からのNO<sub>x</sub>の放出速度は一定ではなく、酸素濃度が低下した直後（還元剤供給開始直後）には急激に比較的多量のNO<sub>x</sub>が放出され、その後はほぼ一様な比較的低い放出速度でNO<sub>x</sub>が放出されることが判明している。この、還元剤供給開始直後にNO<sub>x</sub>吸蔵還元触媒から吸収したNO<sub>x</sub>が急激に放出される現象を「NO<sub>x</sub>の吐き出し」と呼ぶことにして、NO<sub>x</sub>の吐き出しにおけるNO<sub>x</sub>放出量（放出速度）はNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量、すなわちNO<sub>x</sub>吸蔵還元触媒内に吸収されたNO<sub>x</sub>の量が多い程大きくなる。このため、NO<sub>x</sub>吸蔵還元触媒の再生操作を比較的高いNO<sub>x</sub>吸蔵量レベルで実行するようとしているとNO<sub>x</sub>の吐き出しにより放出された多量の未浄化NO<sub>x</sub>により一時的に排気中の還元剤が不足するようになり、還元剤供給開始直後に放出されたNO<sub>x</sub>が未浄化のままNO<sub>x</sub>吸蔵還元触媒下流側に流出するようになる。NO<sub>x</sub>の吐き出しは還元剤供給開始後短時間で終了し、その後はNO<sub>x</sub>放出速度は比較的低い速度になるため吐き出しが終了した後は排気中の還元剤が不足することとはなくなる。このため、NO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量が比較的高いレベルにあっても還元剤供給開始後ある程度の時間が経過すれば未浄化のNO<sub>x</sub>の流出は停止するようになるが、この場合、再生操作実行毎にNO<sub>x</sub>吸蔵還元触媒から未浄化のNO<sub>x</sub>が流出するため全体としての平均NO<sub>x</sub>浄化率をある程度以上には上げることができない問題が生じる。

【0008】更に、NO<sub>x</sub>吸蔵還元触媒では上記NO<sub>x</sub>の吐き出し以外にも「NO<sub>x</sub>の染み出し」と称する現象が発見されている。従来、NO<sub>x</sub>吸蔵還元触媒はNO<sub>x</sub>吸蔵量が飽和量に到達しない限り排気空燃比がリーンであれば排気中のNO<sub>x</sub>を吸収すると考えられていた。しかし、実際にはNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量が増大するにつれてNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸収能力は徐々に低下することが判明している。このため、NO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量が飽和量よりかなり低い状態であっても、NO<sub>x</sub>吸蔵還元触媒下流側には触媒に吸

取されなかったNO<sub>x</sub>が流出している。また、このNO<sub>x</sub>流出量はNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量が多くなるにつれて増大し、NO<sub>x</sub>吸蔵量が飽和量に到達すると排気中のNO<sub>x</sub>はNO<sub>x</sub>吸蔵還元触媒に全く吸収されず下流側に流出するようになる。このように、排気空燃比がリーンのときにNO<sub>x</sub>吸蔵量に応じた量のNO<sub>x</sub>が未浄化のまま触媒下流側に流出する現象を「NO<sub>x</sub>の染み出し」と称する。

【0009】上述のように、NO<sub>x</sub>吸蔵還元触媒の再生時にNO<sub>x</sub>の吐き出しにより流出する未浄化のNO<sub>x</sub>量、及びリーン空燃比下でNO<sub>x</sub>の染み出しにより流出する未浄化のNO<sub>x</sub>量はともにNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量に応じて増大する。このため、従来のようにNO<sub>x</sub>吸蔵量が比較的高いレベルに到達したときにNO<sub>x</sub>吸蔵還元触媒の再生操作を実行するようにした排気浄化装置では、NO<sub>x</sub>の吐き出しと染み出しとにより放出される未浄化のNO<sub>x</sub>のため、ある程度以上には全体としてのNO<sub>x</sub>浄化率を向上させることはできない。

【0010】本発明は上記問題に鑑み、NO<sub>x</sub>の吐き出しままたは染み出しによるNO<sub>x</sub>浄化率の低下を防止し、大幅にNO<sub>x</sub>浄化率を向上させることが可能な内燃機関の排気浄化装置を提供することを目的としている。

#### 【0011】

【課題を解決するための手段】請求項1に記載の発明によれば、内燃機関の排気通路に配置され流入する排気の空燃比がリーンのときに排気中のNO<sub>x</sub>を吸収し、流入する排気中の酸素濃度が低下したときに吸収したNO<sub>x</sub>を放出するNO<sub>x</sub>吸蔵還元触媒と、該NO<sub>x</sub>吸蔵還元触媒に流入する排気空燃比がリーンのときにNO<sub>x</sub>吸蔵還元触媒に還元剤を供給することにより、NO<sub>x</sub>吸蔵還元触媒に流入する排気中の酸素濃度を低下させるとともに、放出されたNO<sub>x</sub>を還元浄化する還元剤供給装置とを備えた内燃機関の排気浄化装置において、前記NO<sub>x</sub>吸蔵還元触媒は、前記還元剤供給開始直後に、供給された還元剤によっては還元されない未浄化NO<sub>x</sub>を下流側に放出し、該未浄化NO<sub>x</sub>量はNO<sub>x</sub>吸蔵還元触媒の吸収したNO<sub>x</sub>量に応じて増加し、前記還元剤供給装置は、NO<sub>x</sub>吸蔵還元触媒に吸収されたNO<sub>x</sub>量が所定のレベルに到達したときにNO<sub>x</sub>吸蔵還元触媒に還元剤を供給し、前記所定のNO<sub>x</sub>吸収量レベルは、前記還元剤供給開始時の前記NO<sub>x</sub>吸蔵還元触媒からの未浄化NO<sub>x</sub>放出量が予め定めた値以下になるように設定されていることを特徴とする内燃機関の排気浄化装置が提供される。

【0012】すなわち、請求項1に記載の発明ではNO<sub>x</sub>吸蔵還元触媒に吸収されたNO<sub>x</sub>量が所定レベルに到達する毎にNO<sub>x</sub>吸蔵還元触媒の再生操作が行われる。しかし、この所定レベルは再生操作開始時のNO<sub>x</sub>の吐き出しにより流出する未浄化のNO<sub>x</sub>量が所定の低い値に維持されるように、従来に較べてかなり低いレベルに

設定される。これにより、本発明では従来に比較して非常に短い間隔で再生操作が実行されることになるが、再生操作開始時の吐き出しによる未浄化のNO<sub>x</sub>の放出量は極めて低い値に抑えられるため全体としてのNO<sub>x</sub>の浄化率を大幅に向上させることができる。なお、NO<sub>x</sub>吸蔵還元触媒への還元剤の供給はNO<sub>x</sub>吸蔵還元触媒上流側の排気通路に炭化水素(HC)等から成る還元剤を噴射することによって行っててもよいし、機関を短時間リッチ空燃比で運転することにより、排気中の未燃HC、CO成分を増大させることによって行っても良い。

【0013】請求項2に記載の発明によれば、内燃機関の排気通路に配置され流入する排気の空燃比がリーンのときに排気中のNO<sub>x</sub>を吸収し、流入する排気中の酸素濃度が低下したときに吸収したNO<sub>x</sub>を放出するNO<sub>x</sub>吸蔵還元触媒と、該NO<sub>x</sub>吸蔵還元触媒に流入する排気空燃比がリーンのときにNO<sub>x</sub>吸蔵還元触媒に還元剤を供給することにより、NO<sub>x</sub>吸蔵還元触媒に流入する排気中の酸素濃度を低下させるとともに、放出されたNO<sub>x</sub>を還元浄化する還元剤供給装置とを備えた内燃機関の排気浄化装置において、前記NO<sub>x</sub>吸蔵還元触媒は、流入する排気空燃比がリーンであっても吸収したNO<sub>x</sub>量に応じて増大する量の未浄化のNO<sub>x</sub>を下流側に放出し、前記還元剤供給装置は、NO<sub>x</sub>吸蔵還元触媒に吸収されたNO<sub>x</sub>量が所定のレベルに到達したときにNO<sub>x</sub>吸蔵還元触媒に還元剤を供給し、前記所定のNO<sub>x</sub>吸収量レベルは、リーン空燃比排気下における前記NO<sub>x</sub>吸蔵還元触媒からの未浄化NO<sub>x</sub>放出量が予め定めた値以下になるように設定されていることを特徴とする内燃機関の排気浄化装置が提供される。

【0014】すなわち、請求項2に記載の発明においてもNO<sub>x</sub>吸蔵還元触媒に吸収されたNO<sub>x</sub>量が所定レベルに到達する毎にNO<sub>x</sub>吸蔵還元触媒の再生操作が行われる。しかし、本発明ではこの所定レベルはNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量の増大によるNO<sub>x</sub>の染み出しにより流出する未浄化のNO<sub>x</sub>量が所定の低い値に維持されるように、従来に較べてかなり低いレベルに設定される。これにより、本発明では従来に比較して非常に短い間隔で再生操作が実行されることになるが、NO<sub>x</sub>の染み出しによる未浄化のNO<sub>x</sub>の放出量は極めて低い値に抑えられるため全体としてのNO<sub>x</sub>の浄化率を大幅に向上させることができる。なお、本発明においてもNO<sub>x</sub>吸蔵還元触媒への還元剤の供給は排気通路への還元剤の噴射により、または機関を短時間リッチ空燃比で運転することにより、行っても良い。

【0015】なお、NO<sub>x</sub>吸蔵還元触媒の再生操作を開始するNO<sub>x</sub>吸蔵量のレベルは、請求項1の発明の吐き出しによる未浄化NO<sub>x</sub>量が所定値以下になる値、または本発明の染み出しによる未浄化NO<sub>x</sub>量が所定値以下になる値のいずれか低い方の値に設定するようにすれば、より完全に未浄化のNO<sub>x</sub>の放出を低減することが

できる。

【0016】請求項3に記載の発明によれば、前記還元剤供給装置は、前記NO<sub>x</sub>吸蔵還元触媒の上流側の排気通路に還元剤を噴射する還元剤供給ノズルを備え、NO<sub>x</sub>吸蔵還元触媒に流入する排気空燃比がリーンのときにNO<sub>x</sub>吸蔵還元触媒に吸収されたNO<sub>x</sub>量が前記所定のレベルに到達する毎に予め定めた量の還元剤を排気中に供給する請求項1または請求項2に記載の内燃機関の排気浄化装置が提供される。

10 【0017】すなわち、請求項3に記載の発明ではNO<sub>x</sub>吸蔵還元触媒への還元剤の供給はNO<sub>x</sub>吸蔵還元触媒上流側の排気通路に配置した還元剤供給ノズルから排気中に還元剤を噴射することにより行われる。これにより、リッチ空燃比で運転することが困難なディーゼル機関においてもNO<sub>x</sub>の浄化率を大幅に向上させることができる。

【0018】請求項4に記載の発明によれば、前記還元剤供給ノズルからの還元剤の噴射量と噴射率とは、前記還元剤の供給が行われる時間間隔に応じて設定されている請求項3に記載の内燃機関の排気浄化装置が提供される。すなわち、請求項4に記載の発明では、再生操作の実行間隔に応じて還元剤供給ノズルからの還元剤の噴射率と噴射量とが設定される。本発明では、従来に較べて短い間隔で再生操作が実行されることになるため、各再生操作時に従来と同じ量の還元剤を噴射していたのでは還元剤消費量が大幅に増大する。また、本発明ではNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量が低いレベルにあるときに再生操作を行うため、再生操作に必要とされる還元剤の量は少ない。このため、本発明では再生操作時に供給

20 30 40 50 する還元剤の量は再生操作の時間間隔に応じて、すなわち再生操作時にNO<sub>x</sub>吸蔵還元触媒に吸蔵されているNO<sub>x</sub>の量に応じて過不足が生じないように設定される。また、これにより各再生操作時に還元剤供給ノズルから噴射される還元剤の量は減少するが、この少ない量の還元剤を長時間の間に排気に噴射したのでは、還元剤が排気に希釈されてしまいNO<sub>x</sub>吸蔵還元触媒の酸素濃度を低下させる事ができない。そこで、本発明では、還元剤供給ノズルからの還元剤の噴射率を噴射量に応じて(すなわち再生操作の実行間隔に応じて)設定し、排気中の還元剤濃度が充分に高く維持されるようにしている。これにより、再生操作の時間間隔が短く設定されても還元剤の消費量の増大が抑制されるとともに、NO<sub>x</sub>吸蔵還元触媒の完全な再生が行われる。

#### 【0019】

【発明の実施の形態】以下、添付図面を用いて本発明の実施形態について説明する。図1は、本発明の排気浄化装置の一実施形態の概略構成を示す図である。図1において、1は内燃機関を示す。本実施形態では、内燃機関1としてディーゼル機関が使用されており、機関の各気筒排気ポートは排気マニホールド31を介して共通の排気

通路3に接続されている。更に、排気通路3上には後述するNO<sub>x</sub>吸蔵還元触媒7が配置されている。図1に9で示すのはNO<sub>x</sub>吸蔵還元触媒7再生操作時にNO<sub>x</sub>吸蔵還元触媒7に還元剤を供給する還元剤供給装置である。還元剤供給装置は、NO<sub>x</sub>吸蔵還元触媒7の排気入口近傍に配置された還元剤供給ノズル91を備えNO<sub>x</sub>吸蔵還元触媒7に流入する排気中に還元剤を噴射することによりNO<sub>x</sub>吸蔵還元触媒7に流入する排気中の酸素濃度を低下させ、触媒7から吸収したNO<sub>x</sub>を放出させるとともに、放出されたNO<sub>x</sub>を還元浄化する。後述するように、本実施形態では還元剤として機関1の燃料(ディーゼル油)が使用される。還元剤供給装置9は、図示しない機関燃料系統に接続され、燃料系統から供給された加圧燃料を還元剤供給ノズル91から排気通路3内に噴射する。

【0020】図1に30で示すのは、機関1の電子制御ユニット(ECU)である。本実施形態では、ECU30はRAM、ROM、CPUを備えた公知の構成のマイクロコンピュータとして構成され、機関1の燃料噴射量、燃料噴射時期等の基本制御を行う他、還元剤供給装置9を制御して後述するNO<sub>x</sub>吸蔵還元触媒7からのNO<sub>x</sub>の放出及び還元浄化操作(NO<sub>x</sub>吸蔵還元触媒の再生操作)を実施する。

【0021】本実施形態のNO<sub>x</sub>吸蔵還元触媒7は、アルミナ等の担体上に例えばカリウムK、ナトリウムNa、リチウムLi、セシウムCsのようなアルカリ金属、バリウムBa、カルシウムCaのようなアルカリ土類、ランタンLa、セリウムCe、イットリウムYのような希土類から選ばれた少なくとも一つの成分と、白金Ptのような貴金属とを担持したものである。NO<sub>x</sub>吸蔵還元触媒は流入する排気ガスの空燃比がリーンのときに、排気中のNO<sub>x</sub>(NO<sub>2</sub>、NO)を硝酸イオンNO<sub>3</sub><sup>-</sup>の形で吸収し、流入排気ガスの酸素濃度が低下すると吸収したNO<sub>x</sub>を放出するNO<sub>x</sub>の吸放出作用を行う。

【0022】この吸放出のメカニズムについて、以下に白金PtおよびバリウムBaを使用した場合を例にとって説明するが他の貴金属、アルカリ金属、アルカリ土類、希土類を用いても同様なメカニズムとなる。流入排気中の酸素濃度が増大すると(すなわち排気の空燃比がリーン空燃比になると)、これら酸素は白金Pt上にO<sub>2</sub>またはO<sup>2-</sup>の形で付着し、排気中のNO<sub>x</sub>は白金Pt上のO<sub>2</sub>またはO<sup>2-</sup>と反応し、これによりNO<sub>3</sub><sup>-</sup>が生成される。また、流入排気中のNO<sub>x</sub>及び上記により生成したNO<sub>3</sub><sup>-</sup>は白金Pt上で更に酸化されつつ触媒中に吸収されて吸収剤として機能する酸化バリウムBaOと結合しながら硝酸イオンNO<sub>3</sub><sup>-</sup>の形で触媒内に拡散する。このため、リーン雰囲気下では排気中のNO<sub>x</sub>がNO<sub>x</sub>吸蔵還元触媒内に硝酸塩の形で吸収されるようになる。

【0023】また、流入排気中の酸素濃度が低下すると(すなわち、排気の空燃比が低下すると)、白金Pt上でのNO<sub>x</sub>生成量が減少するため反応が逆方向に進むようになり、触媒内の硝酸イオンNO<sub>3</sub><sup>-</sup>はNO<sub>2</sub>の形でNO<sub>x</sub>吸蔵還元触媒から放出されるようになる。この場合、排気中にHC、CO等の成分が存在すると白金Pt上でこれらの成分によりNO<sub>3</sub><sup>-</sup>が還元される。

【0024】本実施形態では、機関1としてディーゼル機関が使用されているため機関の排気空燃比はリーンであり、通常運転中は排気通路3のNO<sub>x</sub>吸蔵還元触媒7にはリーン空燃比の排気が流入し排気中のNO<sub>x</sub>がNO<sub>x</sub>吸蔵還元触媒7に吸収される。また、NO<sub>x</sub>吸蔵還元触媒7上流側の排気通路3に還元剤が供給されるとNO<sub>x</sub>吸蔵還元触媒7には還元剤を含んだ排気が流入し、還元剤の一部はNO<sub>x</sub>吸蔵還元触媒7の白金Pt上で酸素と反応する。これにより、NO<sub>x</sub>吸蔵還元触媒7の雰囲気中の酸素濃度が低下するとともに、還元剤の酸化により未燃HC、CO等の成分が発生する。還元剤の酸化によりNO<sub>x</sub>吸蔵還元触媒7の雰囲気酸素濃度が低下すると、上述したメカニズムによりNO<sub>x</sub>吸蔵還元触媒7からNO<sub>x</sub>が放出され排気中のHC、CO成分により還元される。

【0025】上記NO<sub>x</sub>吸蔵還元触媒からのNO<sub>x</sub>の放出、還元浄化操作(NO<sub>x</sub>吸蔵還元触媒の再生操作)に使用される還元剤としては、排気中でH<sub>2</sub>等の還元成分やHC、CO成分を生成するものが使用され、例えば水素、一酸化炭素等の気体、プロパン、プロピレン、ブタン等の液体又は液体の炭化水素、ガソリン、軽油、灯油等の液体燃料等が使用できる。本実施形態では、内燃機関1としてディーゼル機関が使用されているため、補給、貯蔵の便を考慮して還元剤として機関1の燃料(ディーゼル油)を使用するようしている。還元剤供給装置9は機関1の燃料ポンプ(図示せず)から供給された燃料を遮断弁、流量調整弁(図示せず)を介して還元剤供給ノズル91からNO<sub>x</sub>吸蔵還元触媒7上流側の排気通路に供給することによりNO<sub>x</sub>吸蔵還元触媒7の再生を行う。

【0026】上述のように、NO<sub>x</sub>吸蔵還元触媒7は還元剤供給装置9から還元剤が供給されていないときに(すなわち流入する排気空燃比がリーンのときに)排気中のNO<sub>x</sub>を吸収し、還元剤供給装置9から排気中に還元剤が供給され流入する排気の酸素濃度が低下すると吸収したNO<sub>x</sub>を放出、還元浄化する。このため、従来NO<sub>x</sub>吸蔵還元触媒7が吸収したNO<sub>x</sub>で飽和しない限り下流側には未浄化のNO<sub>x</sub>が放出されることはないと考えられていた。

【0027】ところが、実際の運転ではNO<sub>x</sub>吸蔵還元触媒には前述した「NO<sub>x</sub>の吐き出し」と「NO<sub>x</sub>の染み出し」と称する現象が生じるためNO<sub>x</sub>吸蔵還元触媒が吸収したNO<sub>x</sub>で飽和していない状態でも未浄化のN

$\text{O}_x$  が下流側に放出される場合があることが判明している。本明細書では、前述したように  $\text{NO}_x$  吸収還元触媒の再生操作初期に  $\text{NO}_x$  吸収還元触媒下流側に未浄化の  $\text{NO}_x$  が放出される現象を「 $\text{NO}_x$  の吐き出し」と呼び、 $\text{NO}_x$  吸収還元触媒が排気中の  $\text{NO}_x$  を吸収中（すなわち流入する排気空燃比がリーンのとき）に  $\text{NO}_x$  吸収還元触媒下流側に未浄化の  $\text{NO}_x$  が放出される現象を「 $\text{NO}_x$  の染み出し」と呼び、両者を区別している。

【0028】 $\text{NO}_x$  の吐き出しと染み出しが何故生じるかの理由については現在のことろ明確には判明していないが、以下に説明する現象によるものと推測されている。まず、 $\text{NO}_x$  の吐き出しの生じる理由について説明する。前述のように、 $\text{NO}_x$  吸収還元触媒は吸収した  $\text{NO}_x$  を硝酸塩の形で保持する。このとき、硝酸イオンは  $\text{NO}_x$  吸収還元触媒中の吸収剤（例えば  $\text{BaO}$ ）の表面から内部に拡散により移動して硝酸塩を形成する。このため、 $\text{NO}_x$  の吸収中には吸収剤表面の硝酸イオン濃度は内部の硝酸イオン濃度より高くなっている。この状態で  $\text{NO}_x$  吸収還元触媒の再生操作が開始され吸収剤表面の界面活性素濃度が急激に低下すると、吸収剤表面近傍の高濃度の硝酸イオンが  $\text{NO}_x$  の形で一齊に吸収剤から放出されるようになる。このため、再生操作開始直後には短時間で比較的多量の  $\text{NO}_x$  が  $\text{NO}_x$  吸収還元触媒から放出されるようになり、一時的な還元剤不足が生じ、放出された  $\text{NO}_x$  の一部が未浄化のまま  $\text{NO}_x$  吸収還元触媒下流側に放出されるようになると考えられる。

【0029】吸収剤表面近傍の硝酸イオンが放出された後は、吸収剤内部に保持された硝酸イオンが表面に移動して  $\text{NO}_x$  の形で放出されるようになるが、この場合には吸収剤からの  $\text{NO}_x$  の放出速度は吸収剤内部での硝酸イオンの移動速度に律速されるようになるため、放出速度は比較的低くなり、還元剤の不足は生じない。このため、 $\text{NO}_x$  吸収還元触媒の再生操作開始直後に一時的に未浄化の  $\text{NO}_x$  が下流側に放出される  $\text{NO}_x$  の吐き出しが生じるのである。

【0030】吐き出しにより放出される  $\text{NO}_x$  の量は、吸収剤表面の硝酸イオン濃度が高いほど大きくなる。このため、 $\text{NO}_x$  吸収還元触媒に吸収された  $\text{NO}_x$  量 ( $\text{NO}_x$  吸収量) が多いほど吐き出しにより放出される未浄化の  $\text{NO}_x$  が増大するようになる。また、 $\text{NO}_x$  の染み出しは  $\text{NO}_x$  吸収還元触媒の吸収剤に吸収された  $\text{NO}_x$  量の増大により吸収剤の  $\text{NO}_x$  吸収能力が低下するため生じると考えられる。上述したように、 $\text{NO}_x$  吸収還元触媒の白金 Pt 上で生成された硝酸イオンは吸収剤表面から内部に拡散により移動する。従って、 $\text{NO}_x$  吸収還元触媒の  $\text{NO}_x$  吸収量が増大して吸収剤内部の硝酸イオン濃度が増大すると、内部に硝酸イオンが拡散しにくくなり、吸収剤表面の硝酸イオン濃度が増大する。これにより、白金 Pt 上での  $\text{NO}_x \rightarrow \text{NO}_x^-$  の反応が生じにくくなり排気中の  $\text{NO}_x$  が  $\text{NO}_x$  吸収還元触媒に吸収

されなくなる。このため、 $\text{NO}_x$  吸収還元触媒の  $\text{NO}_x$  吸収中には  $\text{NO}_x$  吸収量が増大するにつれて  $\text{NO}_x$  吸収還元触媒に吸収されず下流側に流出する未浄化の  $\text{NO}_x$  量が増大するようになる。

【0031】また、 $\text{NO}_x$  吸収還元触媒の最大  $\text{NO}_x$  吸収量（飽和量）はリーン空燃比下においても空燃比が低下するにつれて（リッチ側になるにつれて）低下する。このため、 $\text{NO}_x$  吸収還元触媒に比較的多量の  $\text{NO}_x$  が吸収されている場合、運転条件の変化により排気空燃比が低下して  $\text{NO}_x$  吸収還元触媒の飽和量が低下した場合には、飽和量を越える分の吸収  $\text{NO}_x$  は  $\text{NO}_x$  吸収還元触媒から放出されるようになる。従って、例え排気がリーン空燃比であり  $\text{NO}_x$  吸収還元触媒が  $\text{NO}_x$  を吸収中であっても空燃比が低下すると  $\text{NO}_x$  吸収還元触媒から飽和量を越えた分の  $\text{NO}_x$  が放出されるようになる。この場合、当然  $\text{NO}_x$  吸収還元触媒の  $\text{NO}_x$  吸収量が多い程放出される未浄化の  $\text{NO}_x$  量も増大するようになる。

【0032】本実施形態では、 $\text{NO}_x$  吸収還元触媒の  $\text{NO}_x$  吸収中に生じる上記2つの種類の未浄化  $\text{NO}_x$  放出を併せて  $\text{NO}_x$  の染み出しと称している。ところで、 $\text{NO}_x$  の吐き出しと染み出しにより放出される未浄化の  $\text{NO}_x$  の量は、いずれも  $\text{NO}_x$  吸収還元触媒の  $\text{NO}_x$  吸収量が増大するにつれて多くなる。このため、従来のように  $\text{NO}_x$  吸収還元触媒の  $\text{NO}_x$  吸収量が比較的高い値に到達する毎に再生操作を実行するようになっていたのは、 $\text{NO}_x$  の吐き出しと染み出しにより放出される未浄化の  $\text{NO}_x$  量が大きくなってしまい、全体としての  $\text{NO}_x$  処理率を充分に向上させることができない場合がある。

【0033】そこで、本実施形態では従来  $\text{NO}_x$  吸収還元触媒の  $\text{NO}_x$  飽和量を基準にして設定されていた（例えば飽和量の70パーセント）再生操作実行要否判定のための  $\text{NO}_x$  吸収量を、 $\text{NO}_x$  吸収還元触媒からの  $\text{NO}_x$  の吐き出しまだ染み出しにより放出される未浄化の  $\text{NO}_x$  量が所定値以下になるように低い値に設定することにより未浄化の  $\text{NO}_x$  の放出を防止して、 $\text{NO}_x$  吸収還元触媒の全体としての  $\text{NO}_x$  処理率を大幅に向上させている。

【0034】本実施形態では、予め実験により  $\text{NO}_x$  吸収還元触媒の  $\text{NO}_x$  吸収量と  $\text{NO}_x$  の吐き出し、染み出しによる未浄化の  $\text{NO}_x$  放出量との関係を求めておく。そして、この関係から両方の未浄化  $\text{NO}_x$  放出量の合計が予め定めた値以下になる  $\text{NO}_x$  吸収量の最大値（再生操作実行判定値）を定めておき、実際の運転では  $\text{NO}_x$  の吸収量がこの再生操作実行判定値に到達する毎に  $\text{NO}_x$  吸収還元触媒の再生操作を実行する。 $\text{NO}_x$  の吐き出しと染み出しによる未浄化  $\text{NO}_x$  の放出量の許容値は、全体としての  $\text{NO}_x$  処理率（すなわち、ある期間における  $\text{NO}_x$  処理率の平均値）が所望の値になるように設定されるが、従来達成可能な  $\text{NO}_x$  処理率より大幅に

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高い浄化率を達成するために、本実施形態では未浄化のNO<sub>x</sub>の放出量の許容値は極めて小さく設定される。このため、本実施形態ではNO<sub>x</sub>吸蔵還元触媒の再生操作は極めて低い値（例えば飽和量の10パーセント以下の程度）に設定され、従来に較べて極めて短い間隔でNO<sub>x</sub>吸蔵還元触媒の再生操作が実行されるようになる。これにより、NO<sub>x</sub>吸蔵還元触媒再生操作開始直後に吐き出しにより放出される未浄化NO<sub>x</sub>量、及びNO<sub>x</sub>吸蔵量の増大のためにNO<sub>x</sub>吸収中に染み出しにより放出される未浄化NO<sub>x</sub>量が低い値に抑制されるようになる。また、機関運転条件の変化により排気空燃比が低下した場合にも吸蔵NO<sub>x</sub>量が飽和量を越えることがないため、空燃比変化による未浄化のNO<sub>x</sub>放出も防止されるようになる。

【0035】図2は本実施形態の排気浄化装置における浄化率向上の効果を説明するタイミング図である。図2の実線は、本実施形態の排気浄化装置のように短い間隔で再生操作を実行した場合のNO<sub>x</sub>吸蔵還元触媒7出口における排気中のNO<sub>x</sub>濃度を、点線は従来の排気浄化装置のように比較的長い間隔で再生操作を実行した場合のNO<sub>x</sub>吸蔵還元触媒7出口における排気中のNO<sub>x</sub>濃度をそれぞれ示している。また、図2の直線IはNO<sub>x</sub>吸蔵還元触媒7に流入する排気中のNO<sub>x</sub>濃度を示している（図2では、流入排気中のNO<sub>x</sub>濃度が一定の場合を示す）。

【0036】まず、従来の排気浄化装置（点線）の場合について説明すると、従来は比較的NO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量が大きな値に増大するまで再生操作が実行されない。このため、NO<sub>x</sub>吸蔵還元触媒の吸蔵量が増大するにつれて染み出しによる未浄化NO<sub>x</sub>放出量が増大し、図2点線にAで示すように出口排気ガス中のNO<sub>x</sub>濃度が徐々に増大して行く。また、NO<sub>x</sub>吸蔵量が所定値（例えば飽和量の70パーセント程度）に到達すると、還元剤が供給されNO<sub>x</sub>吸蔵還元触媒の再生操作が実行されるが（図2点線、B点）、この場合も再生操作実行時のNO<sub>x</sub>吸蔵量が比較的大きいため、再生操作開始時に吐き出しにより多量の未浄化NO<sub>x</sub>が放出されてしまう（図2点線、C部分）。吐き出しによる未浄化のNO<sub>x</sub>の放出は短時間で終了し、再生が完了するとNO<sub>x</sub>吸蔵還元触媒の出口NO<sub>x</sub>濃度は低下するが、その後NO<sub>x</sub>吸蔵量が増大するにつれて再び出口NO<sub>x</sub>濃度は増大する（図2点線、D部分）。このため従来の排気浄化装置では、全体として図2点線の下側の部分の面積に相当する比較的多量の未浄化NO<sub>x</sub>がNO<sub>x</sub>吸蔵還元触媒下流側に放出されてしまうことになり、全体としてのNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>浄化率は低くなってしまう。

【0037】これに対して、本実施形態の排気浄化装置（図2実線）ではNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量が極めて低い値に到達する毎に短い間隔で再生操作（図2

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実線、B'点）が実行される。このため、NO<sub>x</sub>吸収中の染み出しによる未浄化のNO<sub>x</sub>放出（図2実線、A'部分）及び再生操作実行開始時の吐き出しによる未浄化のNO<sub>x</sub>放出（図2実線、C'）はともに小さな値になる。これにより、全体としてNO<sub>x</sub>吸蔵還元触媒から放出される未浄化のNO<sub>x</sub>量は、図2実線下側部分の面積に相当する極めて少ない量になり、従来の排気浄化装置（図2、点線）に較べて大幅に全体としてのNO<sub>x</sub>浄化効率が向上するようになる。

10 【0038】図3は、本実施形態の上記NO<sub>x</sub>吸蔵還元触媒再生操作を説明するフローチャートである。本操作は、ECU30により一定時間毎に実行されるルーチンにより実施される。図3において、ステップ301では現在のNO<sub>x</sub>吸蔵還元触媒7のNO<sub>x</sub>吸蔵量CNOXが算出される。

【0039】本実施形態では、NO<sub>x</sub>吸蔵量CNOXは機関の運転状態に基づいて算出される。機関から単位時間（例えば図3の操作の実行間隔）あたりに発生するNO<sub>x</sub>量は、機関負荷条件（例えば燃料噴射量と回転数と）により定まる。そこで、本実施形態では、予め機関を負荷条件を変えて運転し、各負荷条件下でのNO<sub>x</sub>発生量を実測し、例えば燃料噴射量と回転数とを用いた数値テーブルの形でECU30のROMに格納してある。ステップ301では、操作実行毎にECU30により別途実行される燃料噴射量演算ルーチンで算出される燃料噴射量と、機関回転数とから上記数値テーブルを用いて前回操作実行時から今回操作実行時までに機関から発生したNO<sub>x</sub>量を算出する。そして、この発生量に所定の定数（排気中のNO<sub>x</sub>のうちNO<sub>x</sub>吸蔵還元触媒7に吸収されるNO<sub>x</sub>の割合）を乗じた値をCNOXに加算する。これにより、CNOXの値はNO<sub>x</sub>吸蔵還元触媒7に吸蔵されたNO<sub>x</sub>量に対応した値となる。

【0040】なお本実施形態では、燃料噴射量と回転数とに応じて算出した値をNO<sub>x</sub>吸蔵還元触媒7のNO<sub>x</sub>吸蔵量CNOXとして用いているが、例えば、前回再生操作実施後の燃料噴射量の積算値、回転数の積算値、あるいは機関が比較的高回転で定常運転されているような場合には前回再生操作完了後の機関運転時間等をNO<sub>x</sub>吸蔵量CNOXとして用いて計算を簡素化しても良い。

【0041】また、図2に示したようにNO<sub>x</sub>吸蔵還元触媒7のNO<sub>x</sub>吸収中、NO<sub>x</sub>吸蔵還元触媒7出口における排気中のNO<sub>x</sub>濃度は染み出しのためNO<sub>x</sub>吸蔵還元触媒のNO<sub>x</sub>吸蔵量に応じて増大していく。このため、例えばNO<sub>x</sub>吸蔵還元触媒7出口に排気中のNO<sub>x</sub>濃度を検出可能なNO<sub>x</sub>濃度センサを配置して、NO<sub>x</sub>濃度センサで検出したNO<sub>x</sub>濃度をCNOXとして使用するようにしても良い。上記により、NO<sub>x</sub>吸蔵還元触媒7のNO<sub>x</sub>吸蔵量CNOXを算出後、ステップ303では、算出したNO<sub>x</sub>吸蔵量CNOXが所定値CNOX50に到達したか否かが判定される。ここで、CNOX

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は、 $\text{NO}_x$  吸収還元触媒7の染み出しにより放出される未浄化 $\text{NO}_x$  の量 ( $\text{NO}_x$  吸収還元触媒7出口における排気中の $\text{NO}_x$  濃度) が予め定めた値以下になる最大 $\text{NO}_x$  吸収量、または $\text{NO}_x$  吸収還元触媒7再生操作開始時に吐き出しにより放出される未浄化 $\text{NO}_x$  の量 (濃度) が予め定めた量以下になる最大 $\text{NO}_x$  吸収量のうちどちらか小さい値に設定される。なお、放出される未浄化の $\text{NO}_x$  量の許容値は、所望の $\text{NO}_x$  净化率から決定される。また、 $\text{CNOX}_0$  の値は、実際の $\text{NO}_x$  吸収還元触媒7を用いた実験により決定することが好ましい。

【0042】ステップ303で $\text{CNOX} \geq \text{CNOX}_0$  であった場合にはステップ305で還元剤供給装置9の還元剤供給ノズル91から所定量の燃料が噴射され、 $\text{NO}_x$  吸収還元触媒7の再生が行われる。また、再生操作終了後、ステップ305では $\text{NO}_x$  吸収量 $\text{CNOX}$  の値はリセットされる。なお、還元剤供給ノズル91から噴射する還元剤 (本実施形態ではディーゼル油) の噴射量は、 $\text{NO}_x$  吸収還元触媒の $\text{NO}_x$  吸収量 $\text{CNOX}$  の全量を浄化するのに充分な量のHC、CO成分を発生可能な最小量に設定される。このように還元剤供給量を再生操作実行時の $\text{NO}_x$  吸収還元触媒の $\text{NO}_x$  吸収量に応じて設定することにより、本実施形態では一回の再生操作で噴射される還元剤の量は低く抑えられる。このため、本実施形態では極めて短い時間間隔で再生操作を行なうにとかわらず、還元剤の消費量は従来に較べて僅かに (すなわち、従来未浄化のまま放出されていた $\text{NO}_x$  を浄化するのに使用される還元剤の量に相当する量だけ) 増大する程度になる。また、本実施形態では極めて短い時間間隔で再生操作が実行されるため、短時間で所要量の還元剤をノズル91から噴射する必要がある。また、1回の再生操作で噴射される還元剤の量は比較的僅かなので、長い時間をかけてこの少量の還元剤を噴射したのでは、噴射された還元剤が排気により希釈されてしまい排気中の還元剤濃度を充分に上昇させることができなくな

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る。そこで、本実施形態では、還元剤供給ノズル91からの還元剤の噴射量は再生操作の実行間隔 (再生操作開始時の $\text{NO}_x$  吸収量) に応じて設定し、更にノズル91からの噴射率は噴射量及び再生操作実行間隔との両方を考慮して設定するようしている。これにより、1回の再生操作で必要とされる量の還元剤を必要とされる濃度で $\text{NO}_x$  吸収還元触媒に流入する排気中に供給することが可能となる。

【0043】なお、本実施形態では還元剤供給ノズル91

から還元剤を $\text{NO}_x$  吸収還元触媒に供給しているが、排気による希釈を防止し充分な濃度の還元剤を $\text{NO}_x$  吸収還元触媒7に到達させるためには還元剤供給ノズル91を $\text{NO}_x$  吸収還元触媒7上流側にできるだけ近接した位置に配置することが望ましい。

【0044】

【発明の効果】各請求項に記載の発明によれば、 $\text{NO}_x$  吸収還元触媒からの $\text{NO}_x$  の吐き出しや染み出しによる未浄化 $\text{NO}_x$  のために排気浄化効率が低下することを防じ、排気浄化効率を大幅に向上させることが可能となる共通の効果を奏する。

【図面の簡単な説明】

【図1】本発明をディーゼル機関に適用した実施形態の概略構成を示す図である。

【図2】本発明による $\text{NO}_x$  净化率の向上の効果を説明する図である。

【図3】本発明による $\text{NO}_x$  吸収還元触媒の再生操作の一実施形態を説明するフローチャートである。

【符号の説明】

- 1 … ディーゼル機関
- 2 … 排気通路
- 3 …  $\text{NO}_x$  吸収還元触媒
- 4 … 還元剤供給装置
- 30 … 電子制御ユニット (ECU)
- 91 … 還元剤供給ノズル

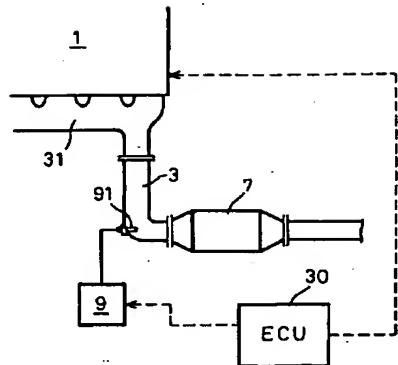
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【図1】

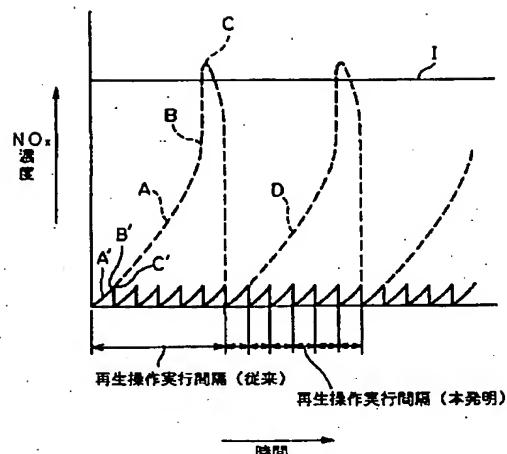
図1



1…ディーゼル機関  
3…排気通路  
7…NO<sub>x</sub>吸収還元触媒  
9…還元剤供給装置  
30…電子制御ユニット  
91…還元剤供給ノズル

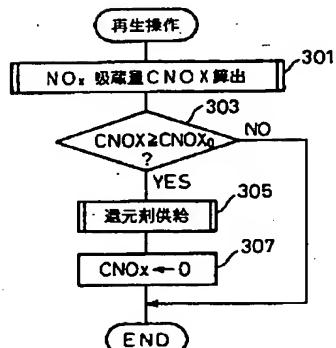
【図2】

図2



【図3】

図3



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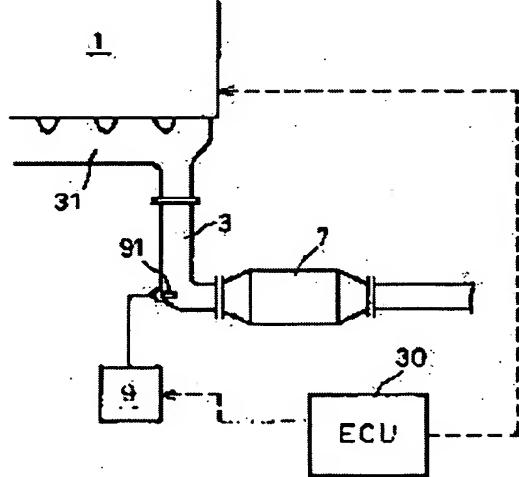
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## (54) EXHAUST GAS EMISSION CONTROL DEVICE FOR INTERNAL COMBUSTION ENGINE

### (57) Abstract:

**PROBLEM TO BE SOLVED:** To improve the NOX purification efficiency of an NOX occlusion reduction catalyst.

**SOLUTION:** An NOX occlusion reduction catalyst 7 is arranged in the exhaust passage 3 of an engine 1 to absorb NOX contained in exhaust gas of an engine under lean air-fuel ratio operation. When an NOX occlusion amount of the catalyst 7 attains a predetermined decision value, a reducing agent (diesel oil) is injected in an exhaust passage on the upper stream side of the catalyst 7 through a reducing agent feed nozzle 91 and NOX is emitted from the catalyst 7 for reduction purification. The decision value is set such that an emission amount of unpurified NOX due to exudation under absorption of NOX is decreased to a predetermined low value. This constitution, since emission of unpurified NOX through discharge or exudation owing to the increase of an occlusion NOX amount is suppressed to a low value, remarkably improves the NOX purification efficiency of the whole of the NOX occlusion reduction catalyst.



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## CLAIMS

## [Claim(s)]

[Claim 1] NOX under exhaust air when an air-fuel ratio of exhaust air which is arranged in an internal combustion engine's flueway and flows is Lean NOX absorbed when it absorbed and an oxygen density under flowing exhaust air fell NOX to emit An occlusion reduction catalyst This NOX It is NOX when an exhaust air air-fuel ratio which flows into an occlusion reduction catalyst is Lean. By supplying a reducing agent to an occlusion reduction catalyst, it is NOX. NOX emitted while reducing an oxygen density under exhaust air which flows into an occlusion reduction catalyst A reducing-agent feeder which carries out reduction purification It is the exhaust emission control device of an internal combustion engine having the above, and is said NOX. An occlusion reduction catalyst Un-purifying [ which is not returned immediately after said reducing-agent supply initiation depending on a supplied reducing agent / NOX ]. It emits to the downstream. Un-purifying [ this / NOX ]. An amount is NOX. NOX which an occlusion reduction catalyst absorbed It increases according to an amount. Said reducing-agent feeder NOX NOX absorbed by occlusion reduction catalyst It is NOX when an amount reaches predetermined level. A reducing agent is supplied to an occlusion reduction catalyst, and it is said predetermined NOX. Absorbed amount level Said NOX at the time of said reducing-agent supply initiation Un-purifying [ NOX ] from an occlusion reduction catalyst. It is characterized by being set up so that it may become below the value that a burst size defined beforehand.

[Claim 2] NOX under exhaust air when an air-fuel ratio of exhaust air which is arranged in an internal combustion engine's flueway and flows is Lean NOX absorbed when it absorbed and an oxygen density under flowing exhaust air fell NOX to emit An occlusion reduction catalyst This NOX It is NOX when an exhaust air air-fuel ratio which flows into an occlusion reduction catalyst is Lean. By supplying a reducing agent to an occlusion reduction catalyst, it is NOX. NOX emitted while reducing an oxygen density under exhaust air which flows into an occlusion reduction catalyst A reducing-agent feeder which carries out reduction purification It is the exhaust emission control device of an internal combustion engine having the above, and is said NOX. An occlusion reduction catalyst NOX absorbed even if a flowing exhaust air air-fuel ratio was Lean NOX which is not purified [ of an amount which increases according to an amount ] It emits to the downstream. Said reducing-agent feeder NOX NOX absorbed by occlusion reduction catalyst It is NOX when an amount reaches predetermined level. A reducing agent is supplied to an occlusion reduction catalyst, and it is said predetermined NOX. Absorbed amount level Said NOX under Lean air-fuel ratio exhaust air Un-purifying [ NOX ] from an occlusion reduction catalyst. It is characterized by being set up so that it may become below the value that a burst size defined beforehand.

[Claim 3] Said reducing-agent feeder is said NOX. A flueway of the upstream of an occlusion reduction catalyst is equipped with a reducing-agent supply nozzle which injects a reducing agent, and it is NOX. It is NOX when an exhaust air air-fuel ratio which flows into an occlusion reduction catalyst is Lean. NOX absorbed by occlusion reduction catalyst An exhaust emission control device of an internal combustion engine according to claim 1 or 2 supplied while exhausting a reducing agent of an amount beforehand defined whenever an amount reached said predetermined level.

[Claim 4] Injection quantity and an injection rate of a reducing agent from said reducing-agent supply nozzle are an exhaust emission control device of an internal combustion engine according to claim 3 set up according to a time interval to which supply of said reducing agent is performed.

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[Translation done.]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention is NOX under exhaust air about an internal combustion engine's exhaust emission control device when the exhaust air air-fuel ratio which flows into details is Lean. NOX absorbed when it absorbed and the oxygen density under flowing exhaust air fell NOX to emit It is related with the exhaust emission control device of the internal combustion engine having an occlusion reduction catalyst.

[0002]

[Description of the Prior Art] NOX under exhaust air when the flowing exhaust air air-fuel ratio is Lean NOX absorbed when it absorbed and the oxygen density under flowing exhaust air fell NOX to emit The occlusion reduction catalyst is known. This kind of NOX As an example of an internal combustion engine's exhaust emission control device using an occlusion reduction catalyst, there are some which were indicated by JP,6-200738,A, for example.

[0003] The equipment of this official report is NOX to the flueway of the engine which can operate with the Lean air-fuel ratio. An occlusion reduction catalyst is arranged. NOX under exhaust air when the engine is operated with the Lean air-fuel ratio It is made to absorb. NOX NOX of an occlusion reduction catalyst It is NOX when an absorbed amount reaches a predetermined value. While exhausting the hydrocarbon of a liquid or a gas etc., it is made to inject as a reducing agent from the reducing-agent supply nozzle arranged to the flueway of the upstream of an occlusion reduction catalyst. NOX If a reducing agent is supplied to an occlusion reduction catalyst with exhaust air, it is NOX of a reducing agent. Since the oxygen density under exhaust air falls by oxidation on an occlusion reduction catalyst, it is NOX. It is NOX absorbed from the occlusion reduction catalyst. It is emitted. Moreover, emitted NOX On a catalyst, it reacts with the reducing agent under exhaust air, and is returned and purified.

[0004]

[Problem(s) to be Solved by the Invention] However, it is NOX at a certain time interval like the equipment of above-mentioned JP,6-200738,A. A reducing agent is supplied to an occlusion reduction catalyst, and it is NOX. NOX from an occlusion reduction catalyst Depending on the time interval of reducing-agent supply when it is made to perform emission and reduction purification, it is NOX as the whole. The case where the rate of purification does not become good arises.

[0005] Usually, NOX A reducing agent is supplied to an occlusion reduction catalyst, and it is NOX. NOX from an occlusion reduction catalyst Actuation (it is hereafter called "playback actuation of a NOX occlusion reduction catalyst") of performing emission and reduction purification NOX NOX absorbed by the occlusion reduction catalyst It is this NOX, although it performs when fixed level with an amount is reached. The level of an absorbed amount is NOX. NOX which the occlusion reduction catalyst absorbed It is set on the basis of the saturated absorbed amount (saturation content). Namely, NOX of a NOX occlusion reduction catalyst Absorptance is utilized for the maximum and it is NOX. As many NOX(s) as possible in order to stop low the activation frequency of playback actuation of an occlusion reduction catalyst NOX After being absorbed by the occlusion reduction catalyst, it is

desirable to perform playback actuation. Then, NOX which usually performs playback actuation The level of an absorbed amount is NOX. It is set as the comparatively high level (for example, NOX about 70% of saturation content of an occlusion reduction catalyst) which looked at a certain amount of additional coverage to the saturation content of an occlusion reduction catalyst.

[0006] However, it is NOX in this way. NOX of an occlusion reduction catalyst It waits until an absorbed amount reaches comparatively high level, and it is NOX. When playback actuation of an occlusion reduction catalyst is performed, it is NOX as the whole. It has become clear that it is difficult to raise the rate of purification sharply. For example, it is NOX conventionally. At the time of playback actuation of an occlusion reduction catalyst, it is NOX. NOX emitted from the occlusion reduction catalyst It is completely purified by the supplied reducing agent and is NOX which is not purified to the downstream. It was thought that it was not emitted. However, it is NOX in fact. NOX with un-purifying at the time of playback actuation of an occlusion reduction catalyst It has become clear that it may be emitted to the catalyst downstream.

[0007] As mentioned above, it is NOX if a reducing agent is supplied. The oxygen density near the occlusion reduction catalyst falls, and it is NOX. From an occlusion reduction catalyst, it is NOX. It is emitted. however, NOX from a catalyst Rapid comparatively a lot of [ emission speed is not fixed, and / immediately after an oxygen density falls (immediately after reducing-agent supply initiation) ] NOX(s) it emits -- having -- after that -- about -- a comparatively low emission speed which is Mr. one -- NOX It has become clear that it is emitted. It is NOX immediately after this reducing-agent supply initiation. NOX absorbed from the occlusion reduction catalyst It is NOX if the phenomenon emitted rapidly will be called "discharge of NOX". NOX in discharge A burst size (emission speed) is NOX. NOX of an occlusion reduction catalyst The amount of occlusion, i.e., NOX, NOX absorbed in the occlusion reduction catalyst It becomes so large that there are many amounts. For this reason, NOX It is comparatively high NOX about playback actuation of an occlusion reduction catalyst. It is NOX if it is made to perform on the amount level of occlusion. Un-purifying [ which was emitted by discharge / a lot of / NOX ]. NOX which the reducing agents under exhaust air came to run short temporarily, and was emitted immediately after reducing-agent supply initiation It is NOX, having not purified. It comes to flow into the occlusion reduction catalyst downstream. NOX It ends in a short time after reducing-agent supply initiation, and discharge is NOX after that. Since emission speed turns into a comparatively low speed, after discharge is completed, it is lost that the reducing agents under exhaust air run short. For this reason, NOX NOX of an occlusion reduction catalyst It will be non-purified NOX, if a certain amount of time amount passes after reducing-agent supply initiation even if the amount of occlusion is in comparatively high level. An outflow is NOX for every playback actuation activation in this case, although it comes to stop. NOX which is not purified from an occlusion reduction catalyst It is the average NOX as the whole in order to flow out. Above, the problem which cannot be raised produces the rate of purification to some extent.

[0008] furthermore, NOX an occlusion reduction catalyst -- Above NOX except for discharge -- "NOX - oozing out -- " -- \*\* -- the phenomenon to call is discovered. The former and NOX An occlusion reduction catalyst is NOX. If an exhaust air air-fuel ratio is Lean unless the amount of occlusion reaches a saturation content, it is NOX under exhaust air. It was thought that it absorbed. However, it is NOX in fact. NOX of an occlusion reduction catalyst It is NOX as the amount of occlusion increases. NOX of an occlusion reduction catalyst It has become clear that absorptance declines gradually. For this reason, NOX NOX of an occlusion reduction catalyst It is NOX even if it is in the condition that the amount of occlusion is quite lower than a saturation content. NOX which was not absorbed by the catalyst at the occlusion reduction catalyst downstream It is flowing out. Moreover, this NOX A flow is NOX. NOX of an occlusion reduction catalyst It increases as the amount of occlusion increases, and it is NOX. If the amount of occlusion reaches a saturation content, it is NOX under exhaust air. NOX It comes to flow into the downstream, without being absorbed at all by the occlusion reduction catalyst. thus, the time of an exhaust air air-fuel ratio being Lean -- NOX NOX of an amount according to the amount of occlusion the phenomenon which flows into the catalyst downstream, having not purified -- "NOX -- oozing out -- " -- \*\* -- it calls.

[0009] as mentioned above, NOX the time of playback of an occlusion reduction catalyst -- NOX NOX which is not purified [ which flows out by discharge ] the bottom of an amount and the Lean air-fuel ratio -- NOX oozing out -- NOX which is not purified [ flowing out ] an amount -- both -- NOX NOX of an occlusion reduction catalyst It increases according to the amount of occlusion. for this reason, the former -- like -- NOX the time of the amount of occlusion reaching comparatively high level -- NOX the exhaust emission control device which was made to perform playback actuation of an occlusion reduction catalyst -- NOX NOX which is not purified [ which oozes out with discharge and is emitted by \*\* ] a sake -- to some extent -- the above -- NOX as the whole The rate of purification cannot be raised.

[0010] This invention takes an example by the above-mentioned problem, and is NOX. Discharge or NOX depended for oozing out Decline in the rate of purification is prevented and it is NOX sharply. It aims at offering the exhaust emission control device of the internal combustion engine which can raise the rate of purification.

[0011]

[Means for Solving the Problem] NOX under exhaust air [ according to invention according to claim 1 ] when an air-fuel ratio of exhaust air which is arranged in an internal combustion engine's flueway and flows is Lean It absorbs. NOX absorbed when an oxygen density under flowing exhaust air fell NOX to emit An occlusion-reduction catalyst and this NOX It is NOX when an exhaust air air-fuel ratio which flows into an occlusion reduction catalyst is Lean. By supplying a reducing agent to an occlusion reduction catalyst NOX While reducing an oxygen density under exhaust air which flows into an occlusion reduction catalyst Emitted NOX It sets to an exhaust emission control device of an internal combustion engine having a reducing-agent feeder which carries out reduction purification, and is said NOX. An occlusion reduction catalyst Un-purifying [ which is not returned immediately after said reducing-agent supply initiation depending on a supplied reducing agent / NOX ]. It emits to the downstream. Un-purifying [ this / NOX ]. An amount is NOX. NOX which an occlusion reduction catalyst absorbed It increases according to an amount. Said reducing-agent feeder NOX NOX absorbed by occlusion reduction catalyst It is NOX when an amount reaches predetermined level. A reducing agent is supplied to an occlusion reduction catalyst, and it is said predetermined NOX. Absorbed amount level Said NOX at the time of said reducing-agent supply initiation Un-purifying [ NOX ] from an occlusion reduction catalyst. An exhaust emission control device of an internal combustion engine characterized by being set up so that it may become below the value that a burst size defined beforehand is offered.

[0012] That is, by invention according to claim 1, it is NOX. It is NOX whenever the amount of NOX(s) absorbed by occlusion reduction catalyst reaches predetermined level. Playback actuation of an occlusion reduction catalyst is performed. However, this predetermined level is NOX at the time of playback actuation initiation. NOX which is not purified [ which flows out by discharge ] Compared with the former, it is set as quite low level so that an amount may be maintained by low predetermined value. Thereby, since it is stopped by very low value, a burst size of NOX which is not purified according to discharge at the time of playback actuation initiation although playback actuation will be performed at a very short gap in this invention as compared with the former is NOX as the whole. A rate of purification can be raised sharply. In addition, NOX Supply of a reducing agent to an occlusion reduction catalyst may be performed by injecting a reducing agent which changes from a hydrocarbon (HC) etc. to a flueway of the NOX occlusion reduction catalyst upstream, and may be performed by increasing unburnt [ under exhaust air / HC ], and CO component by operating an engine with a short-time rich air-fuel ratio.

[0013] NOX under exhaust air [ according to invention according to claim 2 ] when an air-fuel ratio of exhaust air which is arranged in an internal combustion engine's flueway and flows is Lean It absorbs. NOX absorbed when an oxygen density under flowing exhaust air fell NOX to emit An occlusion reduction catalyst and this NOX It is NOX when an exhaust air air-fuel ratio which flows into an occlusion reduction catalyst is Lean. By supplying a reducing agent to an occlusion reduction catalyst NOX While reducing an oxygen density under exhaust air which flows into an occlusion reduction catalyst Emitted NOX It sets to an exhaust emission control device of an internal combustion engine

having a reducing-agent feeder which carries out reduction purification, and is said NOX. An occlusion reduction catalyst NOX absorbed even if a flowing exhaust air air-fuel ratio was Lean NOX which is not purified [ of an amount which increases according to an amount ] It emits to the downstream. Said reducing-agent feeder NOX NOX absorbed by occlusion reduction catalyst It is NOX when an amount reaches predetermined level. A reducing agent is supplied to an occlusion reduction catalyst, and it is said predetermined NOX. Absorbed amount level Said NOX under Lean air-fuel ratio exhaust air Unpurifying [ NOX ] from an occlusion reduction catalyst. An exhaust emission control device of an internal combustion engine characterized by being set up so that it may become below the value that a burst size defined beforehand is offered.

[0014] That is, it also sets to invention according to claim 2, and is NOX. NOX absorbed by occlusion reduction catalyst It is NOX whenever an amount reaches predetermined level. Playback actuation of an occlusion reduction catalyst is performed. however -- this invention -- this predetermined level -- NOX NOX of an occlusion reduction catalyst NOX by increase of the amount of occlusion oozing out -- NOX which is not purified [ flowing out ] Compared with the former, it is set as quite low level so that an amount may be maintained by low predetermined value. Thereby, it is NOX although playback actuation will be performed at a very short gap in this invention as compared with the former. NOX which is not purified [ which is depended for oozing out ] Since it is stopped by very low value, a burst size is NOX as the whole. A rate of purification can be raised sharply. In addition, it also sets to this invention and is NOX. Supply of a reducing agent to an occlusion reduction catalyst is good in a line injection of a reducing agent to a flueway, or by operating an engine with a short-time rich air-fuel ratio.

[0015] In addition, NOX NOX which starts playback actuation of an occlusion reduction catalyst Level of the amount of occlusion is un-purifying [ NOX ] according to discharge of invention of claim 1. Unpurifying [ a value from which an amount becomes below a predetermined value, or / of this invention / which is depended for oozing out / NOX ]. It will completely be non-purified NOX if it is made for the direction [ a value from which an amount becomes below a predetermined value is low either ] to set it as a value. Emission can

[0016] According to invention according to claim 3, said reducing-agent feeder Said NOX A flueway of the upstream of an occlusion reduction catalyst is equipped with a reducing-agent supply nozzle which injects a reducing agent. NOX It is NOX when an exhaust air air-fuel ratio which flows into an occlusion reduction catalyst is Lean. NOX absorbed by occlusion reduction catalyst Whenever an amount reaches said predetermined level, an exhaust emission control device of an internal combustion engine according to claim 1 or 2 supplied while exhausting a reducing agent of an amount defined beforehand is offered.

[0017] That is, by invention according to claim 3, it is NOX. Supply of a reducing agent to an occlusion reduction catalyst is NOX. It is carried out by injecting a reducing agent during exhaust air from a reducing-agent supply nozzle arranged to a flueway of the occlusion reduction catalyst upstream. Operating with a rich air-fuel ratio also sets to a difficult Diesel engine by this, and it is NOX. A rate of purification can be raised sharply.

[0018] According to invention according to claim 4, an exhaust emission control device of an internal combustion engine according to claim 3 by which injection quantity and an injection rate of a reducing agent from said reducing-agent supply nozzle are set up according to a time interval to which supply of said reducing agent is performed is offered. That is, in invention according to claim 4, an injection rate and injection quantity of a reducing agent from a reducing-agent supply nozzle are set up according to an activation gap of playback actuation. Since playback actuation will be performed at a short gap in this invention compared with the former, in having injected a reducing agent of the amount same at the time of each playback actuation as the former, reducing-agent consumption increases sharply. Moreover, at this invention, it is NOX. NOX of an occlusion reduction catalyst When the amount of occlusion is in low level, in order to perform playback actuation, there are few amounts of a reducing agent needed for playback actuation. For this reason, an amount of a reducing agent supplied in this invention at the time of playback actuation responds to a time interval of playback actuation, namely, is NOX at the time of

playback actuation. NOX by which occlusion is carried out to an occlusion reduction catalyst It is set up so that excess and deficiency may not arise according to an amount. Moreover, a reducing agent will be diluted with having injected a reducing agent of this small amount to exhaust air between long times, although it decreased by exhaust air, and an amount of a reducing agent injected from a reducing-agent supply nozzle by this at the time of each playback actuation is NOX. An oxygen density of an occlusion reduction catalyst cannot be reduced. so, in this invention, an injection rate of a reducing agent from a reducing-agent supply nozzle is set up according to injection quantity (namely, an activation gap of playback actuation -- responding), and reducing-agent concentration under exhaust air is made to be maintained highly enough. It is NOX while increase of consumption of a reducing agent is controlled by this, even if a time interval of playback actuation is set up short. Perfect playback of an occlusion reduction catalyst is performed.

[0019]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained using an accompanying drawing. Drawing 1 is drawing showing the outline configuration of 1 operation gestalt of the exhaust emission control device of this invention. In drawing 1, 1 shows an internal combustion engine. With this operation gestalt, the Diesel engine is used as an internal combustion engine 1, and each gas column exhaust air port of an engine is connected to the common flueway 3 through the exhaust manifold 31. Furthermore, NOX later mentioned on a flueway 3 The occlusion reduction catalyst 7 is arranged. It is NOX which 9 shows to drawing 1. It is NOX at the time of occlusion reduction catalyst 7 playback actuation. It is the reducing-agent feeder which supplies a reducing agent to the occlusion reduction catalyst 7. A reducing-agent feeder is NOX. It has the reducing-agent supply nozzle 91 arranged near the exhaust air entrance of the occlusion reduction catalyst 7, and is NOX. It is NOX by injecting a reducing agent during the exhaust air which flows into the occlusion reduction catalyst 7. NOX which the oxygen density under exhaust air which flows into the occlusion reduction catalyst 7 was reduced, and was absorbed from the catalyst 7 NOX emitted while making it emit Reduction purification is carried out. With this operation gestalt, the fuel for an engine 1 (Diesel oil) is used as a reducing agent so that it may mention later. It connects with the engine fuel network which is not illustrated, and the reducing-agent feeder 9 injects the pressurization fuel supplied from the fuel system in a flueway 3 from the reducing-agent supply nozzle 91.

[0020] It is an engine's 1 electronic control unit (ECU) which 30 shows to drawing 1. At this operation gestalt, ECU30 is NOX which it is constituted as a microcomputer of a well-known configuration of having had RAM, ROM, and CPU, and basic control, such as an engine's 1 fuel oil consumption and fuel injection timing, is performed, and also controls and mentions the reducing-agent feeder 9 later. NOX from the occlusion reduction catalyst 7 Emission and reduction purification actuation (NOX playback actuation of an occlusion reduction catalyst) are carried out.

[0021] NOX of this operation gestalt The occlusion reduction catalyst 7 is Potassium K, Sodium Na, Lithium Li, and Caesium Cs on support, such as an alumina. Alkali metal [ like ], Barium Ba, and calcium calcium At least one component chosen from rare earth like an alkaline earth [ like ], Lanthanum La, Cerium Ce, and Yttrium Y and noble metals like Platinum Pt are supported. NOX An occlusion reduction catalyst is nitrate ion NO<sub>3</sub> about NOX under exhaust air (NO<sub>2</sub>, NO), when the air-fuel ratio of the flowing exhaust gas is Lean. - NOX which absorbed in the form, and was absorbed when the oxygen density of inflow exhaust gas fell NOX to emit An absorption/emission action is performed.

[0022] It becomes the same mechanism even if it uses other noble metals, alkali metal, an alkaline earth, and rare earth, although the mechanism of this absorption/emission is explained taking the case of the case where Platinum Pt and Barium Ba are used, below. if the oxygen density under inflow exhaust air increases (namely, -- if the air-fuel ratio of exhaust air turns into the Lean air-fuel ratio) -- these oxygen -- Platinum Pt top -- O<sub>2</sub>- or the form of O<sub>2</sub>- adhering -- NOX under exhaust air O<sub>2</sub>- on Platinum Pt or O<sub>2</sub>- reacting -- thereby -- NO<sub>2</sub> It is generated. Moreover, NO<sub>2</sub> under inflow exhaust air And NO<sub>2</sub> generated by the above It is nitrate ion NO<sub>3</sub>, combining with the barium oxide BaO which is absorbed in a catalyst and functions as an absorbent oxidizing further on Platinum Pt. - It is spread in a catalyst in a

form. For this reason, under lean atmosphere, it is NOX under exhaust air. NOX It comes to be absorbed in the form of a nitrate in an occlusion reduction catalyst.

[0023] moreover -- if the oxygen density under inflow exhaust air falls (namely, -- if the air-fuel ratio of exhaust air falls) -- NO2 on Platinum Pt in order that the amount of generation may decrease -- a reaction -- hard flow -- progressing -- coming -- nitrate ion NO3- within a catalyst NO2 a form -- NOX It comes to be emitted from an occlusion reduction catalyst. In this case, when components, such as HC and CO, exist during exhaust air, it is NO2 by these components on Platinum Pt. It is returned.

[0024] Since the Diesel engine is used as an engine 1 with this operation gestalt, an engine's exhaust air air-fuel ratio is Lean, and it is usually NOX of a flueway 3 during operation. Exhaust air of the Lean air-fuel ratio flows into the occlusion reduction catalyst 7, and it is NOX under exhaust air. NOX It is absorbed by the occlusion reduction catalyst 7. Moreover, NOX It is NOX if a reducing agent is supplied to the flueway 3 of the occlusion reduction catalyst 7 upstream. Exhaust air containing a reducing agent flows into the occlusion reduction catalyst 7, and some reducing agents are NOX. It reacts with oxygen on the platinum Pt of the occlusion reduction catalyst 7. thereby -- NOX while the oxygen density in the ambient atmosphere of the occlusion reduction catalyst 7 falls -- oxidation of a reducing agent -- unburnt -- components, such as HC and CO, occur. It is NOX by oxidation of a reducing agent. If the ambient atmosphere oxygen density of the occlusion reduction catalyst 7 falls, it is NOX by the mechanism mentioned above. NOX is emitted from the occlusion reduction catalyst 7, and it is returned by HC under exhaust air, and CO component.

[0025] Above NOX NOX from an occlusion reduction catalyst as the reducing agent used for emission and reduction purification actuation (NOX playback actuation of an occlusion reduction catalyst) -- under exhaust air -- it is -- H2 etc. -- what generates a reduction component, and HC and CO component is used, for example, liquid fuel, such as a hydrocarbon of liquids, such as gases, such as hydrogen and a carbon monoxide, a propane, a propylene, and butane, or a gas, a gasoline, gas oil, and kerosene, etc. can be used. Since the Diesel engine is used as an internal combustion engine 1, he is trying to use the fuel for an engine 1 (Diesel oil) as a reducing agent in consideration of the facilities of supply and storage with this operation gestalt. The reducing-agent feeder 9 minds a latching valve and a flow control valve (not shown) for the fuel supplied from an engine's 1 fuel pump (not shown), and is NOX from the reducing-agent supply nozzle 91. It is NOX by supplying the flueway of the occlusion reduction catalyst 7 upstream. The occlusion reduction catalyst 7 is reproduced.

[0026] As mentioned above, NOX The occlusion reduction catalyst 7 is NOX under exhaust air (namely, when the flowing exhaust air air-fuel ratio is Lean) when the reducing agent is not supplied from the reducing-agent feeder 9. NOX which was absorbed, and was absorbed when the oxygen density of the exhaust air which a reducing agent is supplied during exhaust air and flows from the reducing-agent feeder 9 fell Reduction purification is emitted and carried out. For this reason, it is NOX conventionally. NOX which the occlusion reduction catalyst 7 absorbed Unless it is saturated, it is NOX which is not purified to the downstream. It was thought that it was not emitted.

[0027] however -- actual operation -- NOX "the discharge of NOX" mentioned above in the occlusion reduction catalyst, and "NOX -- oozing out -- " -- \*\* -- since the phenomenon to call arises -- NOX NOX which the occlusion reduction catalyst absorbed NOX which is not purified in the condition of not being saturated, either It has become clear that it may be emitted to the downstream. It is NOX as mentioned above on these specifications. It is NOX in early stages of [ playback actuation ] an occlusion reduction catalyst. NOX which is not purified to the occlusion reduction catalyst downstream The phenomenon emitted "Discharge of NOX", and a call, NOX NOX which an occlusion reduction catalyst is exhausting under absorption (namely, when the flowing exhaust air air-fuel ratio is Lean) -- NOX NOX which is not purified to the occlusion reduction catalyst downstream the phenomenon emitted -- "NOX -- oozing out -- " -- a call and both are distinguished.

[0028] NOX Although it has not become clear clearly now about the reason of why it oozes with discharge and \*\* arises, what is depended on the phenomenon of explaining below is conjectured. First, NOX The reason which discharge produces is explained. As mentioned above, NOX An occlusion reduction catalyst is absorbed NOX. It holds in the form of a nitrate. At this time, nitrate ion is NOX. It

moves to the interior by diffusion from the surface of the absorbent in an occlusion reduction catalyst (for example, BaO), and a nitrate is formed. For this reason, NOX During absorption, the nitrate ion concentration on the surface of an absorbent is higher than internal nitrate ion concentration. It is NOX in this condition. When playback actuation of an occlusion reduction catalyst is started and the ambient atmosphere oxygen density on the surface of an absorbent falls rapidly, the high-concentration nitrate ion near the absorbent surface is NO<sub>2</sub>. It comes to be emitted from an absorbent all at once in a form. For this reason, comparatively a lot of [ in a short time ] NOX(s) immediately after playback actuation initiation NOX NOX to which it came to be emitted from an occlusion reduction catalyst, and temporary lack of a reducing agent arose and was emitted It is NOX, with a part not purified. It is thought that it comes to be emitted to the occlusion reduction catalyst downstream.

[0029] The nitrate ion held inside the absorbent after the nitrate ion near the absorbent surface was emitted moves to the surface, and it is NO<sub>2</sub>. Although emitted [ come ] in a form, it is NO<sub>2</sub> from an absorbent in this case. In order to carry out rate-limiting [ of the emission speed ] to the passing speed of the nitrate ion inside an absorbent, emission speed becomes comparatively low and lack of a reducing agent is not produced. For this reason, NOX NOX by which non-purified NOX is temporarily emitted to the downstream immediately after playback actuation initiation of an occlusion reduction catalyst Discharge arises.

[0030] NOX emitted by discharge An amount becomes so large that the nitrate ion concentration on the surface of an absorbent is high. For this reason, NOX NOX absorbed by the occlusion reduction catalyst NOX which is not purified [ which is emitted by discharge, so that there are many amounts (the amount of NOX occlusion) ] It comes to increase. moreover, NOX oozing out -- NOX NOX absorbed by the absorbent of an occlusion reduction catalyst increase of an amount -- NOX of an absorbent It is thought that it is generated in order that occlusion capacity may decline. It is NOX as mentioned above. The nitrate ion generated on the platinum Pt of an occlusion reduction catalyst moves to the interior by diffusion from the absorbent surface. Therefore, NOX NOX of an occlusion reduction catalyst If the amount of occlusion increases and the nitrate ion concentration inside an absorbent increases, it will be hard coming to spread nitrate ion inside, and the nitrate ion concentration on the surface of an absorbent will increase. Thereby, it is NO<sub>2</sub> → NO<sub>3</sub> on Platinum Pt. - It is hard coming to generate a reaction and is NOX under exhaust air. NOX It will not be absorbed by the occlusion reduction catalyst. For this reason, NOX NOX of an occlusion reduction catalyst During absorption, it is NOX. It is NOX as the amount of occlusion increases. NOX which is not purified [ which is not absorbed by the occlusion reduction catalyst but flows into the downstream ] An amount comes to increase.

[0031] moreover, NOX the max of an occlusion reduction catalyst -- NOX as for the amount of occlusion (saturation content), an air-fuel ratio falls to the bottom of the Lean air-fuel ratio -- it takes [ it is alike and ] and falls (as it is on a rich side). For this reason, NOX Comparatively a lot of NOX(s) to an occlusion reduction catalyst When occlusion is carried out, an exhaust air air-fuel ratio falls by change of a service condition, and it is NOX. Occlusion NOX of the part which exceeds a saturation content when the saturation content of an occlusion reduction catalyst falls NOX It comes to be emitted from an occlusion reduction catalyst. Therefore, metaphor exhaust air is the Lean air-fuel ratio, and it is NOX. It is NOX, if an air-fuel ratio falls even if an occlusion reduction catalyst is absorbing NOX. NOX of the part which exceeded the saturation content from the occlusion reduction catalyst It comes to be emitted. In this case, naturally it is NOX. NOX of an occlusion reduction catalyst NOX which is not purified [ which is emitted, so that there are many amounts of occlusion ] An amount also comes to increase.

[0032] At this operation gestalt, it is NOX. NOX of an occlusion reduction catalyst Un-purifying [ of the two above-mentioned classes produced during absorption / NOX ]. Emission is combined and it is NOX. It oozed and \*\* is called. By the way, NOX NOX which is not purified [ which oozes out with discharge and is emitted by \*\* ] Each amount is NOX. NOX of an occlusion reduction catalyst It increases as the amount of occlusion increases. For this reason, it is NOX like before. NOX of an occlusion reduction catalyst It is [ that it is made to perform playback actuation whenever the amount of occlusion reaches a comparatively high value, and ] NOX. NOX which is not purified [ which oozes out with discharge and is emitted by \*\* ]. An amount becomes large and it is NOX as the whole. The rate of purification may

fully be raised.

[0033] So, at this operation gestalt, it is NOX conventionally. NOX of an occlusion reduction catalyst NOX for the playback (for example, 70% of saturation content) actuation activation necessity judging set up on the basis of the saturation content The amount of occlusion NOX NOX from an occlusion reduction catalyst discharge -- or -- oozing out -- NOX which is not purified [ which is emitted ] setting it as a low value so that an amount may become below a predetermined value -- non-purified NOX Emission is prevented. NOX NOX as the whole occlusion reduction catalyst The rate of purification is raised sharply.

[0034] At this operation gestalt, it is NOX by experiment beforehand. NOX of an occlusion reduction catalyst The discharge of the amount of occlusion, and NOX, and NOX which is not purified [ which is depended for oozing out ] It asks for relation with a burst size. And un-purifying [ of this relation to both / NOX ]. NOX from which the sum total of a burst size becomes below the value defined beforehand The maximum (playback actuation activation decision value) of the amount of occlusion is defined, and it is NOX by actual operation. It is NOX whenever the amount of occlusion reaches this playback actuation activation decision value. Playback actuation of an occlusion reduction catalyst is performed. NOX Un-purifying [ NOX ] according to [ ooze out with discharge and ] \*\*. The allowed value of a burst size is NOX as the whole. Although it is set up so that the rate of purification (namely, NOX in a certain period the average of the rate of purification) may become a desired value, it is NOX which can be attained conventionally. NOX which is not purified with this operation gestalt in order to attain the rate of purification sharply higher than the rate of purification The allowed value of a burst size is set up very small. For this reason, at this operation gestalt, it is NOX. It is set as a very low value (for example, 10 or less % of degree of a saturation content), it compares with the former, and playback actuation of an occlusion reduction catalyst is NOX at a very short gap. Playback actuation of an occlusion reduction catalyst comes to be performed. thereby -- NOX Un-purifying [ which is emitted by discharge immediately after occlusion reduction catalyst playback actuation initiation / NOX ]. An amount and NOX an increase of the amount of occlusion sake -- NOX under absorption -- oozing out -- un-purifying [ which is emitted / NOX ] An amount comes to be controlled by the low value. Moreover, it is Occlusion NOX also when an exhaust air air-fuel ratio falls by change of an engine service condition. NOX which is not purified according to air-fuel ratio change in order that an amount may not exceed a saturation content Emission also comes to be prevented.

[0035] Drawing 2 is a timing chart explaining the effect of the improvement in the rate of purification in the exhaust emission control device of this operation gestalt. The continuous line of drawing 2 is NOX at the time of performing playback actuation at a short gap like the exhaust emission control device of this operation gestalt. NOX under exhaust air in occlusion reduction catalyst 7 outlet It is NOX when a dotted line performs playback actuation for concentration at a comparatively long gap like the conventional exhaust emission control device. NOX under exhaust air in occlusion reduction catalyst 7 outlet Concentration is shown, respectively. Moreover, the straight line I of drawing 2 is NOX. NOX under exhaust air which flows into the occlusion reduction catalyst 7 Concentration is shown (at drawing 2, it is NOX under inflow exhaust air the case where concentration is fixed is shown).

[0036] First, if the case of the conventional exhaust emission control device (dotted line) is explained, it is NOX comparatively conventionally. NOX of an occlusion reduction catalyst Playback actuation is not performed until the amount of occlusion increases to a big value. For this reason, NOX Un-purifying [ which is depended for oozing out as the amount of occlusion of an occlusion reduction catalyst increases / NOX ]. As a burst size increases and A shows to the drawing 2 dotted line, it is NOX in outlet exhaust gas. Concentration increases gradually and goes. Moreover, NOX If the amount of occlusion reaches a predetermined value (for example, about 70% of a saturation content), a reducing agent is supplied and it is NOX. Although playback actuation of an occlusion reduction catalyst is performed (the drawing 2 dotted line, B point), it is NOX at the time of playback actuation activation also in this case. Since the amount of occlusion is comparatively large, they are a lot of un-purifying by discharge at the time of playback actuation initiation. It will be emitted (the drawing 2 dotted line, C portion) Emission of NOX which is not purified according to discharge is NOX, if it ends for a short

time and playback is completed. Outlet NOX of an occlusion reduction catalyst Concentration is NOX after that, although it falls. It is Outlet NOX again as the amount of occlusion increases. Concentration increases (the drawing 2 dotted line, D portion). For this reason, un-purifying [ which is equivalent to the area of the portion of the drawing 2 dotted line bottom as a whole in the conventional exhaust emission control device / comparatively a lot of / NOX ]. NOX It will be emitted to the occlusion reduction catalyst downstream, and is NOX as the whole. NOX of an occlusion reduction catalyst The rate of purification will become low.

[0037] On the other hand, with the exhaust emission control device ( drawing 2 continuous line) of this operation gestalt, it is NOX. NOX of an occlusion reduction catalyst Whenever the amount of occlusion reaches a very low value, playback actuation (the drawing 2 continuous line, B' point) is performed at a short gap. For this reason, NOX NOX which is not purified [ which is depended for oozing out ] under absorption NOX which is not purified according to the discharge at the time of emission (the drawing 2 continuous line, A' portion) and playback actuation activation initiation Both emission (the drawing 2 continuous line, C') becomes a small value. Thereby, it is NOX as a whole. NOX which is not purified [ which is emitted from an occlusion reduction catalyst ] It becomes a very small amount equivalent to the area of the drawing 2 continuous line lower part, it compares with the conventional exhaust emission control device ( drawing 2 , dotted line), and an amount is NOX as the whole sharply. Purification effectiveness comes to improve.

[0038] Drawing 3 is the above NOX of this operation gestalt. It is a flow chart explaining occlusion reduction catalyst regeneration actuation. This actuation is carried out by the routine performed by ECU30 for every fixed time amount. It sets to drawing 3 and is the present NOX at step 301. NOX of the occlusion reduction catalyst 7 The amount CNOX of occlusion is computed.

[0039] At this operation gestalt, it is NOX. The amount CNOX of occlusion is computed based on an engine's operational status. The amount of NOX(s) generated from an engine in per [ unit time amount (for example, activation gap of actuation of drawing 3 ) ] becomes settled according to engine load conditions (for example, fuel oil consumption and a rotational frequency). Then, with this operation gestalt, load conditions are changed, an engine is operated beforehand, and it is NOX under each load conditions. An yield is surveyed, for example, it has stored in ROM of ECU30 in the form of the numerical table using fuel oil consumption and a rotational frequency. The fuel oil consumption computed in step 301 by the fuel-oil-consumption operation routine separately performed by ECU30 for every actuation activation, and NOX generated from the engine by the time of actuation activation last time this time from the time of actuation activation using an engine rotational frequency to the above-mentioned numerical table An amount is computed. And the value which multiplied this yield by the predetermined constant (NOX among NOX(s) under exhaust air NOX absorbed by the occlusion reduction catalyst 7 comparatively) is added to CNOX. Thereby, the value of CNOX is NOX. NOX by which occlusion was carried out to the occlusion reduction catalyst 7 It becomes a value corresponding to an amount.

[0040] In addition, it is NOX about the value computed with this operation gestalt according to fuel oil consumption and a rotational frequency. NOX of the occlusion reduction catalyst 7 Although used as an amount CNOX of occlusion, when the addition value of the fuel oil consumption after playback actuation implementation, the addition value of a rotational frequency, or the engine is comparatively operated steadily by high rotation last time, for example, it is NOX about the engine operation time after the completion of playback actuation etc. last time. It may use as an amount CNOX of occlusion, and count may be simplified.

[0041] Moreover, it is NOX as shown in drawing 2 . NOX of the occlusion reduction catalyst 7 Under absorption and NOX NOX under exhaust air in occlusion reduction catalyst 7 outlet Concentration oozes out and, for a \*\* reason, is NOX. NOX of an occlusion reduction catalyst It increases according to the amount of occlusion. For this reason, NOX NOX under exhaust air to occlusion reduction catalyst 7 outlet NOX which can detect concentration NOX which has arranged the concentration sensor and was detected by the NOX concentration sensor You may make it use concentration as CNOX. By the above, it is NOX. NOX of the occlusion reduction catalyst 7 NOX computed at step 303 after computing the

amount CNOX of occlusion. The amount CNOX of occlusion is the predetermined value CNOX0. It is judged whether it reached or not. here -- CNOX0 NOX the occlusion reduction catalyst 7 -- oozing out - un-purifying [ which is emitted / NOX ] the max from which an amount (NOX NOX under exhaust air in occlusion reduction catalyst 7 outlet concentration) becomes below the value defined beforehand -- NOX the amount of occlusion -- or NOX Un-purifying [ which is emitted by discharge at the time of occlusion reduction catalyst 7 playback actuation initiation / NOX ]. the max from which an amount (concentration) turns into below the amount defined beforehand -- NOX the inside of the amount of occlusion -- either -- it is set as a small value. In addition, NOX which is not purified [ which is emitted ] The allowed value of an amount is desired NOX. It is determined from the rate of purification. Moreover, CNOX0 A value is actual NOX. It is desirable to determine by the experiment using the occlusion reduction catalyst 7.

[0042] step 303 -- CNOX>=CNOX0 it was -- to a case, the fuel of the specified quantity injects from the reducing-agent supply nozzle 91 of the reducing-agent feeder 9 at step 305 -- having -- NOX Playback of the occlusion reduction catalyst 7 is performed. Moreover, after playback actuation termination and at step 305, it is NOX. The value of the amount CNOX of occlusion is reset. In addition, the injection quantity of the reducing agent (this operation gestalt Diesel oil) injected from the reducing-agent supply nozzle 91 is NOX. NOX of an occlusion reduction catalyst It is set as the minimal dose which can generate HC of sufficient amount to purify the whole quantity of the amount CNOX of occlusion, and CO component. Thus, it is NOX at the time of playback actuation activation about the reducing-agent amount of supply. NOX of an occlusion reduction catalyst By setting up according to the amount of occlusion, the amount of the reducing agent injected by one playback actuation is low stopped with this operation gestalt. for this reason, with this operation gestalt, in spite of performing playback actuation with a very short time interval, the consumption of a reducing agent becomes the degree to which only the amount equivalent to the amount of the reducing agent used for purifying NOX currently conventionally emitted with un-purifying namely, -- increases slightly compared with the former. Moreover, with this operation gestalt, since playback actuation is performed with a very short time interval, it is necessary to inject the reducing agent of requirements from a nozzle 91 for a short time. Since the amounts of the reducing agent injected by one playback actuation are comparatively few, the injected reducing agent will be diluted with having injected this little reducing agent over long time amount by exhaust air, and it becomes impossible moreover, to fully raise the reducing-agent concentration under exhaust air. Then, according to the activation gap (NOX at the time of playback actuation initiation the amount of occlusion) of playback actuation, he sets up the injection quantity of the reducing agent from the reducing-agent supply nozzle 91, and is trying to set up the injection rate from a nozzle 91 further with this operation gestalt in consideration of both the injection quantity and a playback actuation activation gap. It is NOX at the concentration for which the reducing agent of the amount needed by one playback actuation is needed by this. It becomes possible to supply during the exhaust air which flows into an occlusion reduction catalyst.

[0043] In addition, at this operation gestalt, it is NOX about the reducing-agent supply nozzle 91 to a reducing agent. Although the occlusion reduction catalyst is supplied, dilution by exhaust air is prevented, and it is NOX about the reducing agent of sufficient concentration. In order to make the occlusion reduction catalyst 7 reach, it is NOX about the reducing-agent supply nozzle 91. It is desirable to arrange in the location which approached the occlusion reduction catalyst 7 upstream as much as possible.

[0044]

[Effect of the Invention] According to invention given in each claim, it is NOX. NOX from an occlusion reduction catalyst Un-purifying [ discharge or / which are depended for oozing out / NOX ]. It prevents that exhaust air purification effectiveness falls to a sake, and the common effect it becomes possible whose to raise exhaust air purification effectiveness sharply is done so.

[Translation done.]